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# PATENT SPECIFICATION

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 (72) Inventor SIEGMAR LAUFER



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## (54) PROCESS FOR HYDROPHOBISING HIGHLY DISPERSE OXIDES OF METALS AND/OR OF SILICON

(71) We, DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER, a body corporate organised under the laws of Germany of 9 Weissfrauenstrasse, 6 Frankfurt Main 1, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for hydrophobising highly disperse oxides of metals and/or of silicon by treating the oxide particles with organo silicon compounds in the presence of ammonia as catalyst.

It is known that finely divided, precipitated or pyrogenic silicas can be rendered permanently hydrophobic by chemically modifying their surface.

Whereas conventional processes for hydrophobising precipitated silicas are based on a slurry technique, in which a variety of different hydrophobising agents derived from silicon compounds are used, hydrophobising processes in heterogeneous gas phase differing with advantage from the slurry technique have been used for hydrophobising highly disperse pyrogenic silicas.

Thus, silicas obtained pyrogenically for example by the process disclosed in DAS 1,163,784 can be converted immediately after production into hydrophobic finely divided fillers in a fluidised bed following the production process, for example by means of alkyl chlorosilanes.

According to an earlier proposal, silicas which have been thermally activated are also hydrophobised in heterogeneous gas phase at elevated temperature by means of volatile alkyl siloxanes or alkyl siloxanes which have been brought into the gas phase, for example D<sub>4</sub> (octamethylcyclotetrasiloxane).

According to another proposal, silicas, irrespective of the method by which they have been produced, are converted after activation into finely divided hydrophobic products by means of alkyl or aryl-alkoxy silanes or alkyl/aryl-alkoxy siloxanes, the alkyl/aryl-alkoxy silanes or alkyl/aryl alkoxy siloxanes required as hydrophobising agents being used either in the gas phase or even in heterogeneous gas phase in the form of a spray mist.

Although the first two of the aforementioned processes give satisfactory products, they do involve considerable technical outlay in terms of apparatus. By contrast, the last of the aforementioned processes has the considerable advantage that the outlay which it involves in terms of apparatus is in fact minimal. The small quantities of alcohols which still adhere to the products, despite full utilisation of the minimal outlay in terms of apparatus, are generally harmless. Nevertheless, it would be desirable to obtain with minimal technical outlay hydrophobic products which are substantially free from volatile constituents emanating from the production process.

However, it is possible to use as hydrophobising agents alkyl-alkoxy silanes or alkyl-alkoxy siloxanes of the kind whose alkoxy radicals are derived from particularly volatile alcohols, for example methanol. However, experience has shown that hydrophobic silicas produced with alkoxy derivatives derived from higher alcohols show superior properties. This advantage is inevitably offset by the disadvantage that the higher alcohols liberated during hydrophobising are difficult and, in some cases, impossible completely to remove from the end product, even the most minute quantities

[Price 25p]

being regarded as harmful solely from the point of view of the noxious odours which they give off.

On the other hand, particularly effective hydrophobic properties in silicas can also be obtained by hydrophobising with alkyl-alkoxy silanes containing fairly long alkyl chains. In this case, however, lower alcohols are best used for the alkoxy radical purely on account of the rapid increase in boiling points with the length of the alkyl chain.

In addition to this, the alkyl-(or aryl) alkoxy silanes which can be used for hydrophobising silicas react more slowly, the more carbon atoms present in their alkyl radicals on the one hand and the more carbon atoms present in their alkoxy radicals on the other hand.

Accordingly, alkyl-alkoxy silanes or alkyl-alkoxy siloxanes with carbon chains longer than  $C_2$  require such long reaction times at normal temperature, even in cases where very highly active or highly active silicas are used (in the absence of catalytically effective substances), that they cannot be considered for use in this most simple form, at least so far as large-scale application is concerned.

By contrast, according to an earlier proposal, they can be used with advantage for a large-scale hydrophobising process in cases where a trace of HCl, for example 0.1% of the hydrophobising agent used, is simultaneously added. In this way, hydrophobic silicas are obtained over periods ranging from a few minutes up to one hour in dependence both upon the type of alkyl-alkoxy silanes or alkyl-alkoxy siloxanes used and upon their alkyl and alkoxy radicals.

However, the acid character still adhering to the product after production by the process just described is unfavourable or even completely prevents the product thus prepared from being used in a number of cases, for example for application in silicone rubber.

Although it is also shown in the aforementioned earlier proposal how silicas can be converted with advantage, even in the absence of catalysts, into hydrophobic products by means of alkyl-alkoxy silanes or alkyl-alkoxy siloxanes, this embodiment does necessitate the use of a commercial installation for hydrophobising.

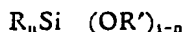
The problem of hydrophobising silicas with alkyl-alkoxy silanes or alkyl-alkoxy siloxanes or cyclo siloxanes, even at room temperature, in the absence of acid catalysts at a speed sufficient for industrial purposes using an uncomplicated process, has hitherto remained unresolved.

Although it is known from United States Patent Specification 3,334,062, that finely divided inorganic materials, including for example silicas with a water content of at least 1% by weight, can be treated with cyclo-trisiloxane in the presence of ammonium compounds, including *inter alia* ammonium hydroxide and ammonium carbonate, at temperatures in the range from 15 to 170°C over a period ranging from 5 minutes up to several hours, resulting in the formation of hydrophobic products suitable for use as fillers in elastomers, rubber and synthetic resins, this process is confined to hydrophobising with cyclo trisiloxanes because treatment with cyclo tetrasiloxanes, for example  $D_4$ , does not lead to hydrophobic, but instead to distinctly hydrophilic products.

The present invention provides a process for hydrophobising finely divided oxides of metals and/or of silicon by treating the oxide particles with an organo silicon compound, for example, an organo alkoxy silane, organo alkoxy siloxane or organo cyclo-siloxane in the presence of ammonia as catalyst, which process, despite its simplicity, gives completely and permanently hydrophobic products which are neutral and completely free from volatile constituents, including alcohols without any need for acid catalysts to be used, and in which it is possible although not necessarily essential to use both linear organo siloxanes, such as for example hexamethyldisiloxane ( $D_2$ ), and also cyclic organo siloxanes such as for example hexamethyl cyclo trisiloxane ( $D_3$ ) or octamethyl cyclo tetrasiloxane ( $D_4$ ).

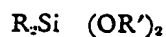
According to the invention the oxide particles are activated by treatment at a temperature of from 700 to 1000°C over a period of 60 seconds or less with a gas stream which is inert to the acids in a fluidised bed or with a stream of a gas which is inert to the oxide flowing in countercurrent, the particles, completely freed from water, are then treated with an organo silicon compound, a stream of dry ammonia gas being allowed to act upon the oxide particles for a period of 60 seconds or less, before, during or after their treatment with the organo silicon compound.

From the group of organo alkoxy silanes, compounds corresponding to the following general formula may be used:



in which each R represents an alkyl radical with 1 to 12 carbon atoms or an aryl radical and each R' represents an alkyl radical with 1 to 8 carbon atoms, whilst  $n$  is a number from 1 to 3.

Included in this group are organo alkoxysilanes of the general formulae

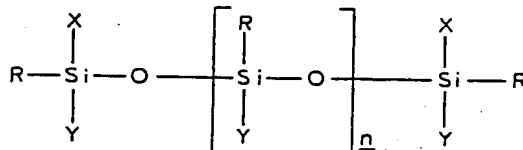


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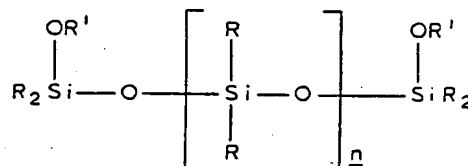
in which R and R' are as defined above.

From the group of organo alkoxy siloxanes or organo alkoxy-oligo siloxanes, compounds corresponding to the following general formula may be used:

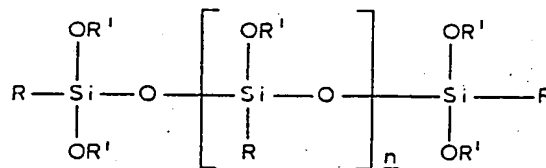


in which each X and Y, which may be the same or different, represent R or OR', each R is an alkyl radical with 1 to 8 carbon atoms or an aryl radical, each R' is an alkyl radical with 1 to 8 carbon atoms, and  $n$  is 0 or 1.

Also included are organo alkoxysiloxanes or organo alkoxy polysiloxanes of the general formula

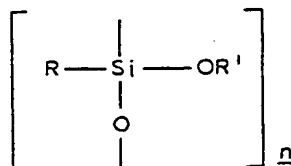


in which each R is an alkyl radical with 1 to 8 carbon atoms or an aryl radical, each R' is an alkyl radical with 1 to 8 carbon atoms, whilst  $n$  is a number from 0 to 2 inclusive; and organo alkoxysiloxanes or organo alkoxyoligosiloxanes of the general formula



in which each R is an alkyl radical with 1 to 12 carbon atoms or an aryl radical, each R' is an alkyl radical with 1 to 8 carbon atoms whilst  $n$  is 0 or 1.

From the group of organo alkoxy-cyclo siloxanes, compounds corresponding to the following general formula may be used:

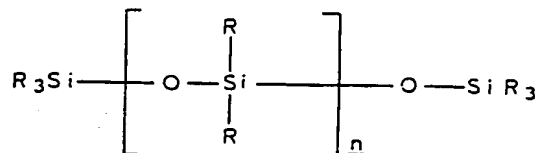


in which each R represents an alkyl radical with 1 to 12 carbon atoms or an aryl radical, each R' represents an alkyl radical with 1 to 8 carbon atoms whilst  $n$  is 3 or 4.

Preferably organoalkoxy silanes or organoalkoxy polysiloxanes are used in which the total of the number of carbon atoms in the radical represented by R plus the number of carbon atoms in the radical represented by R' does not exceed 9. According to one embodiment either the radical R or the radical R' has a number of carbon atoms which is relatively large with respect to the other e.g. one of the radicals R and R' has 3 to 8 carbon atoms whilst the other has 1 to 3 carbon atoms. Thus R may have

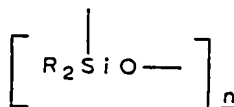
6 to 8 carbon atoms and R' may be CH<sub>3</sub>. Alternatively R may have 3 to 8 carbon atoms and R' 1 to 3 carbon atoms.

The organosilicon compound may also be an organosiloxane of the general formula



5 in which each R represents an alkyl group with 1 to 4 carbon atoms or an aryl radical, whilst  $n$  is a number from 0 to 8. An example of such a siloxane is hexamethyldisiloxane.

In addition an organocyclosiloxane of the formula

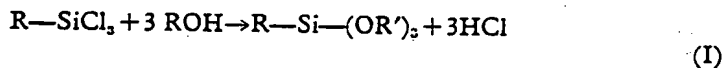


10 in which R represents —CH<sub>3</sub> or —C<sub>2</sub>H<sub>5</sub>, whilst  $n$  is a number from 3 to 5, may be used.

If the finely divided silicas are not activated beforehand by the processes disclosed in British Patent Specification No. 1,292,382 or in British Patent Specification No. 1,337,329, the end products treated in otherwise the same way either show no hydrophobic properties at all or, in cases where increased quantities of hydrophobising agents are used, only inadequate hydrophobic properties.

15 It is possible to use any type of compound from the group of organo siloxanes or organo alkoxy silanes or organo alkoxy siloxanes corresponding to the above general formulae. However, it is of particular advantage to use organo alkoxy silanes or organo alkoxy siloxanes of the kind which can be obtained by reaction with alcohols from organo trihalogen silanes. Since any alcohol and even mixtures of different alcohols can be used as alcoholic component in the production of these organo alkoxy silanes, there is also no need for the organo alkoxy silanes used in accordance with the invention to be in the form of single pure compounds or liquids or even readily volatile, because it is also possible with equal effect to use solids providing they are suitably distributed.

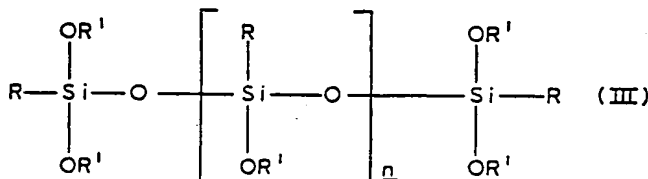
25 Alkyl trichlorosilanes readily react with alcohols in accordance with the following equation:



to form the alkyl-trialkoxy silanes (I), the alkyl-alkoxy siloxanes (II),



and alkyl-alkoxy polysiloxanes (III)



derived from (I) frequently being formed in the same reaction.

35 Both the alkoxy silanes (I) and the siloxanes (II) and (III) can be used for hydrophobising either individually or in admixture with one another.

It is quite remarkable that organo alkoxy polysiloxanes (III), which, depending

upon the alcohols used, are formed as secondary products in relatively small or even in considerable quantities during production of the organo alkoxy silanes, can be used equally effectively.

Surprisingly, the reaction mixture formed during preparation of the organo alkoxy silanes or organo alkoxy polysiloxanes can also be directly used as hydrophobising agent, thus making the process according to the invention considerably more economical because, in this case, the individual reaction products do not have to be separated by complicated operations.

Since the process according to the invention is based on catalysis with ammonia, neutral hydrophobic silicas are obtained in cases where the reaction mixture used for hydrophobising still contains residues of gaseous hydrogen chloride. Accordingly, the organo alkoxy silanes or organo alkoxy-oligo siloxanes do not have to be in the form of commercially pure products for applications in which the small quantities of ammonium chloride simultaneously formed where hydrophobising is carried out with mixtures of this kind, are not harmful.

However, even traces of ammonium chloride are undesirable in cases where the hydrophobic products have to meet more stringent requirements. The alkyl-alkoxy silanes or siloxanes used can be freed from every last trace of HCl and/or chlorosilanes either during production or during separation of the reaction mixture by treatment with ammonia by methods known *per se* which do not form any part of the present invention.

In view of this wide range of application of the process according to the invention, it is obvious that it is possible to resort to those starting materials which can be produced with minimal technical outlay both in the selection of the organo halogen silanes required for producing the hydrophobising agents and also in the choice of the alcohols.

Thus, in the most simple case, a hydrophobic product can be produced by adding the aforementioned hydrophobising agents to the activated silicas accommodated in any type of vessel, for which purpose the hydrophobising agents can either be stirred in, sprayed in, in droplet form or introduced in the vapour phase, optionally in admixture with a gas stream which is inert to the oxide.

Completely hydrophobic products are obtained over periods ranging from a few seconds up to several hours where gaseous  $\text{NH}_3$  is introduced according to the invention. The time required to develop full hydrophobic properties after the ammonia has been introduced depends on the type of hydrophobising agent used, upon the radicals R, and especially R', and upon the temperature. This is extremely surprising because tests have shown that other amines, for example pyridine, or *n*-dibutyl amine do not have any catalytic effect, even after several weeks.

Preferably the organosilicon compound is mixed with the oxide e.g. silica or a mixed oxide, at a temperature above  $20^\circ\text{C}$  although the subsequent treatment with anhydrous ammonia gas can be at normal temperature and normal pressure. As used herein the terms "normal temperature" and "normal pressure" mean room temperature and atmospheric pressure respectively.

It is particularly surprising that, where the more readily volatile alkyl-alkoxy silanes are used, completely hydrophobic products are obtained over periods of from 3 to 30 minutes, even at room temperature. In the context of the invention, more readily volatile alkyl-alkoxy silanes are compounds of the kind whose boiling points at normal pressure are still below approximately  $200^\circ\text{C}$ , in which case the radicals R and R' in the sense of the above general formula can contain up to 6 and 8 carbon atoms providing only R is large and R' small or *vice versa*, for example R contains 6 to 8 carbon atoms and R' is  $\text{CH}_3$ .

In many cases, for example for application in silicone rubber, it is desirable to have a product which is completely free from volatile compounds and, in addition, neutral. This requirement is satisfied by the process according to the invention in an embodiment which uses alkyl-alkoxy silanes which are derived from readily volatile alcohols.

One particularly surprising aspect was that, even in cases where alkyl-alkoxy silanes with a relatively long alkyl chain are used, the silicas activated by the aforementioned processes give completely hydrophobic products in a matter of minutes, even at room temperature, without any need for special technical equipment. Thus, a completely hydrophobic product is obtained in three minutes for example from *n*-hexyl trimethoxy silane and an activated pyrogenic silica following admixture, and can readily be freed, again at room temperature, both from  $\text{NH}_3$  and also from the methanol formed during the reaction by means of gas stream which is inert to the silica in a simple countercurrent moving bed.

In the absence of  $\text{NH}_3$ , treatment of the silicas activated by the aforementioned processes with organo alkoxy silanes at room temperature in the absence of a catalyst only gives completely hydrophobic products after a very long contact time. With organo siloxanes, for example  $\text{D}_4$  (octamethyl cyclo-tetrasiloxane), it is impossible to obtain hydrophobic products even after very long contact times under the same conditions.

Accordingly, it is surprising that completely hydrophobic products can be obtained by the process according to the invention even in cases where organo siloxanes (instead of the organo alkoxy silanes or siloxanes) with similar volatility are used.

Since, in this modification of the process according to the invention, organo groups are situated on the surface of the hydrophobised silicas, it is a welcome addition to the hydrophobised silicas obtainable with organo alkoxy silanes on whose surface organo oxy groups can also be present in addition to organo groups.

It can of course be preferred to work the process according to the invention on a continuous cycle. In this case, the activated silicas are mixed with the aforementioned hydrophobising agents and  $\text{NH}_3$  in a moving bed, as known *per se*.

The reaction mixture then passes through a residence zone which is either relatively short or relatively long according to the considerations referred to above, in order thereafter to be introduced into a countercurrent moving bed in which ammonia and alcohol, if any, are removed by means of a gas stream which is inert to the silica.

Hitherto, it has only been possible to obtain hydrophobic products which are free from volatile compounds and, in addition, react neutrally, by high-temperature hydrophobising techniques.

The process according to the invention is illustrated by the following Examples:

#### EXAMPLE 1

Following activation by the method of British Specification No. 1,292,328, 500 g of a pyrogenic silica (BET surface  $120 \text{ m}^2/\text{g}$ ) were sprayed at normal pressure and at normal temperature, while stirring, with 40 g (8% by weight) of *n*-propyl triisopropoxy silane (MW 248.4).

After 1 hour, a dry  $\text{NH}_3$ -gas stream is directed onto the product for 2 to 3 seconds, after which the product was shaken around a few times.

10 minutes after the ammonia had been directed onto it, the product could no longer be wetted with water.

A sample which was tested before introduction of the ammonia was completely wetted by water.

#### EXAMPLE 2

Following activation by the method of British Patent Specification No. 1,292,328, 500 g of pyrogenic silica (BET surface  $120 \text{ m}^2/\text{g}$ ) were introduced into a vessel, placed under a vacuum and 70 g (14% by weight) of a mixture of  $\text{C}_8$ - $\text{C}_{12}$ -alkyl trimethoxy silane (average MW 220, 36, b.p.,  $54$ — $56^\circ\text{C}$ ) added dropwise for a short time during which the vessel was vigorously shaken. After the vacuum had been eliminated with nitrogen, a dry stream of  $\text{NH}_3$ -gas was introduced into the product for 2 to 3 seconds.

All the manipulations (except for activation) were carried out at normal temperature ( $20^\circ\text{C}$ ).

After 1 hour, the product could no longer be wetted with water and had a specific surface of  $76 \text{ m}^2/\text{g}$  (BET) and a carbon content of 5.86%.

#### EXAMPLE 3

Following activation by the method of British Patent Specification No. 1,292,328, 500 g of a pyrogenic silica (BET surface  $120 \text{ m}^2/\text{g}$ ) were introduced into a vessel, placed under vacuum and 100 g (20% by weight) of *n*-propyl-tris-2-ethylhexoxy silane (MW 458.8; b.p.,  $182$ — $183^\circ\text{C}$ ) preheated to  $50^\circ\text{C}$  added dropwise at room temperature for a short time during which the vessel was vigorously shaken. After the vacuum had been eliminated with nitrogen a stream of dry  $\text{NH}_3$  gas was introduced into the product for 2 to 3 seconds. A sample taken 5 minutes after the ammonia had been passed through was completely hydrophobic. Surface  $70 \text{ m}^2/\text{g}$  (BET), carbon content 7.9%.

#### EXAMPLE 4

Following activation by the method of British Patent Specification No. 1,292,328, 500 g of MOX 80 (BET surface  $80 \text{ m}^2/\text{g}$ ) were admixed while stirring at room temperature with 35 g (7% by weight) of *n*-propyl trimethoxy silane (MW 164.3; b.p.,  $146^\circ\text{C}$ ). MOX 80 is a pyrogenic mixed oxide consisting of  $\text{SiO}_2$ +1% by weight  $\text{Al}_2\text{O}_3$ .

After 5 minutes, a stream of dry  $\text{NH}_3$  gas was introduced into the product for 2 to 3 seconds. A sample which was taken 3 minutes after the ammonia had been passed through was completely hydrophobic.

#### EXAMPLE 5

Following activation by the method of British Patent Specification No. 1,337,329, 500 g of a precipitated silica (BET surface  $150 \text{ m}^2/\text{g}$ ) were sprayed while stirring at room temperature with 75 g (15% by weight) of *n*-propyltri-*n*-butoxy silane (MW 290.5; b.p.:  $97^\circ\text{C}$ ).

After 5 minutes, a stream of dry  $\text{NH}_3$  gas was passed through the mixture for 2 to 3 seconds while stirring. The vessel was then vigorously shaken.

10 minutes after the ammonia had been introduced, the product could no longer be wetted with water.

#### EXAMPLE 6

Following activation by the method of British Patent Specification No. 1,292,328, 500 g of a pyrogenic silica (BET surface  $120 \text{ m}^2/\text{g}$ ) were introduced into a vessel, placed under a vacuum and 75 g (15% by weight) of di-*n*-propyl-tetra-*n*-butoxy disiloxane (MW 530.8; b.p.:  $174-184^\circ\text{C}$ ) preheated to  $60^\circ\text{C}$  quickly added dropwise with shaking at room temperature. After 30 minutes, the vacuum was eliminated at room temperature and a stream of dry  $\text{NH}_3$  gas passed through the mixture for 2 to 3 seconds.

After it had been shaken around, the product was free-flowing. A sample taken after 6 hours was completely hydrophobic.

#### EXAMPLE 7

60 g of  $\text{D}_4$  (octamethyl cyclo-tetrasiloxane) were added dropwise with shaking at normal pressure and at room temperature to 300 g of a pyrogenic silica (surface  $200 \text{ m}^2/\text{g}$ ) previously activated by the method of British Patent Specification No. 1,292,328, after which the vessel was shaken for another 10 minutes.  $\text{NH}_3$  gas was then introduced into the mixture for 2 to 3 seconds during which the vessel was shaken around.

A sample taken after standing for 2 days at room temperature could no longer be wetted with water.

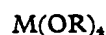
#### EXAMPLE 8

Following activation by the method of British Patent Specification 1,292,328, 500 g of a pyrogenic mixed oxide (BET surface  $80 \text{ m}^2/\text{g}$ ,  $\text{SiO}_2 + 1\%$  by weight  $\text{Al}_2\text{O}_3$ ) were introduced into a vessel, placed under a vacuum and 35 g (7% by weight) of octamethyl cyclo-tetrasiloxane ( $\text{D}_4$ ) sprayed in for a short time while shaking at room temperature ( $20^\circ\text{C}$ ).

After 30 minutes, the vacuum was eliminated with dry nitrogen and a dry stream of  $\text{NH}_3$  gas passed through the mixture for 2 to 3 seconds, a considerable improvement in the flow properties being immediately recognisable.

A sample taken after standing for 3 days at room temperature was completely hydrophobic.

Our copending application 54564/71 (Serial No. 1371218) describes and claims a process for hydrophobising finely divided oxides of metals and/or of silicon by anchoring hydrocarbon radicals in firm chemical linkage to the oxide surface by intensively mixing with the oxide a hydrolysable metal or metalloid compound containing —OR groups, of the general formula



in which M represents an element of the IVth group of the Periodic System whilst each R represents an alkyl radical with 1 to 8 carbon atoms or an aryl radical, it being possible for the radicals R in the same molecule to be the same or different, or with an oligomer of such a compound, the oxide having a water content of less than 1% by weight.

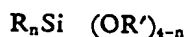
#### WHAT WE CLAIM IS:—

1. A process for hydrophobising finely divided oxides of metals and/or silicon wherein the oxide particles are activated by treatment at a temperature of from  $700$  to  $1,000^\circ\text{C}$  over a period of 60 seconds or less with a gas stream which is inert to the acids in a fluidised bed or with a stream of a gas which is inert to the oxide flowing in countercurrent, the particles, completely freed from water, are then treated with an



organo silicon compound, a stream of dry ammonia gas being allowed to act upon the oxide particles for a period of 60 seconds or less, before, during or after their treatment with the organo silicon compound.

2. A process as claimed in Claim 1, wherein the organo silicon compound used is an organo alkoxy silane corresponding to the general formula

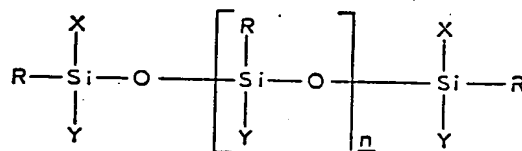


in which each R represents an alkyl radical with 1 to 12 carbon atoms or an aryl radical and each R' represents an alkyl radical with 1 to 8 carbon atoms, whilst  $n$  is a number from 1 to 3.

3. A process as claimed in Claim 2, wherein  $n$  is 2.

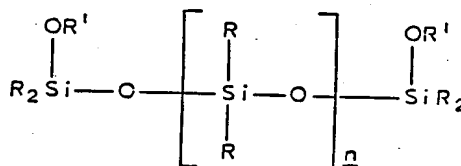
4. A process as claimed in Claim 2, wherein  $n$  is 1.

5. A process as claimed in Claim 1, wherein the organo silicon compound is an organo alkoxy siloxane or organo alkoxy-oligosiloxane corresponding to the general formula



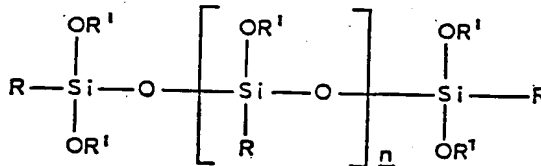
in which each X and Y, which may be the same or different, represent R or OR', each R is an alkyl radical with 1 to 8 carbon atoms or an aryl radical, each R' is an alkyl radical with 1 to 8 carbon atoms, and  $n$  is 0 or 1.

6. A process as claimed in Claim 1, wherein the organo silicon compound is an organo alkoxy siloxane or organo polysiloxane of the general formula



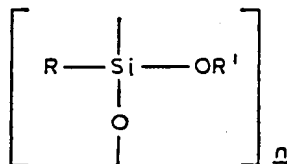
in which each R is an alkyl radical with 1 to 8 carbon atoms or an aryl radical, each R' is an alkyl radical with 1 to 8 carbon atoms, whilst  $n$  is a number from 0 to 2 inclusive.

7. A process as claimed in Claim 1, wherein the organo silicon compound is an organo alkoxy siloxane or organo alkoxy-oligosiloxane of the general formula



in which each R is an alkyl radical with 1 to 12 carbon atoms or an aryl radical, each R' is an alkyl radical with 1 to 8 carbon atoms whilst  $n$  is 0 or 1.

8. A process as claimed in Claim 1, wherein the organo silicon compound is an organo alkoxy-cyclo siloxane corresponding to the general formula



in which each R represents an alkyl radical with 1 to 12 carbon atoms or an aryl radical, each R' represents an alkyl radical with 1 to 8 carbon atoms whilst  $n$  is 3 or 4.

9. A process as claimed in any of Claims 2 to 8, wherein the organo silicon com-

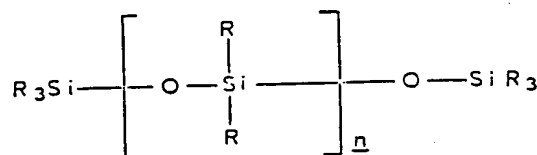
pound is an organo alkoxy silane or organo alkoxy-polysiloxane in which the total of the number of carbon atoms in the radical represented by R plus the number of carbon atoms in the radical represented by R' does not exceed 9.

10. A process as claimed in any of Claims 2 to 9, wherein one of radicals R and R' in the organo alkoxy silane or organo alkoxy-polysiloxane has 3 to 8 carbon atoms whilst the other has 1 to 3 carbon atoms.

11. A process as claimed in Claim 10, wherein the radicals R have a carbon chain of 3 to 8 carbon atoms and the radicals R' have a carbon chain of 1 to 3 carbon atoms.

12. A process as claimed in Claim 11, wherein the radical R contains a carbon chain of 6 to 8 carbon atoms and the radical R' represents CH<sub>3</sub>.

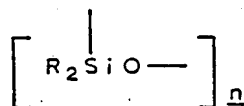
13. A process as claimed in Claim 1, wherein the organo silicon compound is an organo siloxane of the general formula



in which each R represents an alkyl radical with 1 to 4 carbon atoms or an aryl radical, whilst n is a number from 0 to 8.

14. A process as claimed in Claim 13, wherein the organo siloxane is hexamethyl disiloxane.

15. A process as claimed in Claim 1, wherein the organo silicon compound is an organo cyclo siloxane of the general formula



in which R represents —CH<sub>3</sub> or —C<sub>2</sub>H<sub>5</sub> whilst n is a number from 3 to 5.

16. A process as claimed in Claim 15, wherein the organo cyclosiloxane is octamethyl cyclo tetrasiloxane.

17. A process as claimed in any of Claims 1 to 16, wherein the organo silicon compound is mixed with the oxide at a temperature in excess of 20°C.

18. A process as claimed in Claim 17, wherein the oxide mixed at a temperature above 20°C with the organo silicon compound, is treated with anhydrous NH<sub>3</sub> gas at normal temperature.

19. A process as claimed in any of Claims 1 to 16 wherein the organo silicon compound is mixed with the oxide and treated with anhydrous NH<sub>3</sub> gas at normal pressure and at normal temperature.

20. A process for hydrophobising finely divided oxides substantially as herein before described with reference to any of Examples 1 to 8.

21. Hydrophobised finely divided oxides when produced by a process as claimed in any of Claims 1 to 20.

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